On the Physical and Optical Characteristics of CdS Thin Films Deposited by the Chemical Bath Deposition Technique.

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ABSTRACT

Good homogenous cadmium sulfide (CdS) thin films of different thickness were synthesized by using chemical bath deposition (CBD) technique from a bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea unto a glass substrate using different bath compositions. The effect of bath composition on film characteristics were studied using thin film thickness, optical absorption measurement, optical micrograph and XRD spectra. The XRD patterns show that the films have a hexagonal phase with lattice parameter a=b=2.11Å and c=6.7Å, polycrystalline with orientation along different planes and phases and crystallite size for as grown sample are from 12.9nm to 15.4nm. The optical properties and the band gap value reported in this work are in agreement with those obtained by previous studies.

(Keywords: CBD, thin film, adsorption coefficient, CdS, cadmium sulfide, optical properties, energy band gap)

INTRODUCTION

Cadmium sulfide (CdS) films grown by the chemical bath deposition (CBD) method has been used extensively to produce the windows layer in CdS/CdTe solar cell devices. In most cases, this has been carried out by immersing a substrate into a heated bath of reactants in an aqueous solution, typically using ammonia as a complexing agent. Among the several n-type semi-conductor materials, it has been observed that cadmium sulfide (CdS) is the most promising heterojunction partner for the well known polycrystalline photovoltaic materials CdTe and $CuIn(Ga)Se_2$ (CIGS).

Researchers have tried different techniques to investigate structural and optical properties, but the identification of the best electronic quality for photovoltaic applications is challenging due to their film nature of the solar cells (Chaure et al., 2003).

Among techniques that have been used to deposit CdS include electrodeposition (Li et al. 2006; Dharmadasa et al. 2006; Kadirgan et al. 2000; Mirmohseni et al. 2004), vacuum evaporation (Das et al. 1997; Ugwu et al. 2007), screen printing (Makesha et al.2008), photo chemical deposition (Kale et al. 2006), spray pyrolysis (Raji et al. 2005), sputtering (Tsai et al.1996), chemical bath deposition (CBD) (Ximello-Quiebras et al. 2004; Ramaiah et al. 2001; Metin et al. 2008) and Succesive Ionic Layer Adsorption and Reaction (SILAR) (Sartale and Lokhande 2000, 2001; Pathan et al. 2001).

Of all of these methods, the CBD method is the most successful method (Mane and Lokhande 2000) and the highest efficiency CdTe and CIGS solar cells were developed with CBD-CdS layers. Due to the simplicity and the very economical experimental facilities needed in the film deposition, the CBD is the best method to obtain low cost CdS thin films that have optimal features for photovoltaic device applications (Wu et al., 2001).

Deposition of CdS using CBD is based on the slow release of Cd^{2+} ions and S^{2-} ions in aqueous alkali bath and the subsequent condensation of these ions on substrate suitably mounted in the bath. The slow release of Cd^{2+} ions is achieved by adding a complexing agent (ligand) to the Cd salt to form some cadmium complex species which upon dissociation, results in the release of small concentrations of Cd^{2+}ions. The S^{2-} ions are supplied by decomposition of thiourea.

The CdS thin films with low reflectance characteristics in the VIS/NIR regions could be employed in solar thermal control coatings, anti-reflection coating for solar thermal devices and eye glass coating to reduce solar reflectance (Nair et al, 1989). The CdS films for all samples with very low refractive index values could be found useful applications in antireflection coatings.

In this work we report the structural and optical properties of CdS thin films deposited with different bath composition using chemical bath deposition (CBD) technique.

MATERIAL AND METHODS

The CdS films were deposited on microscopic glass slides (25.4mm x 76.2mm x 1.0mm) from a chemical bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea in suitable proportions. The composition of the chemical bath for a set of four representative samples is shown in Table 1.

The bath was maintained under constant stirring using magnetic stirrer at a temperature of 80^{o}C during the deposition. Full details of the CBD deposition of the CdS used is as reported by (Enriquez et al. 2003).

All the solutions were prepared in de-ionized water using analyzed reagents beaker. For us to obtain good adherence and uniformity for the film, it is very important to provide clean substrates to the CBD system. The substrate cleaning was done in the following steps. The glass slide was washed using alkali free detergent and a piece of gauze and rinsed many times in distilled water.

This is followed by ultrasonic cleaning of the glass substrate in an isopropyl alcohol and rinsed many times in de-ionized water. Finally the substrate was dried in air and inserted into the chemical bath.

The substrates were weighed before and after each deposition with the aid of analytical chemical balance and the thin film thickness for sample A, B, C and D was 2,49nm, 4.04nm, 3.69nm and 4.01nm respectively as shown in the Table 2. The sample B and D has high film thickness due to the volume of ammonia (NH_3) concentration in the bath.

A single beam spectrophotometer was used to obtain the spectra absorbance data. Other optical and solid-state properties of the films were obtained by calculations based on theory. X-ray diffraction techniques were used to obtain structural characterization and optical micrograph of the samples were taken.

Table 1: The Composition of the Chemical Bath, Temperature and the Time Duration of the Film Deposition.

Experimental Sample	$CdCl_2$ 0.12mol/l (ml)	NH_4Cl 0.1 mol/l (ml)	NH_3 2 mol/l (ml)	H_2o (ml)	Thiourea 0.3mol/l (ml)	Temp ^{0}C	Time (minutes)
A	3.0	12	15	85	3.0	80	60
B	3.0	12	20	75	3.0	80	60
C	3.0	12	15	75	6.0	80	60
D	3.0	12	20	75	3.0	80	60

Table 2: Mass of Thin Film, Area Covered by Film and Thickness of the Thin Film for Samples A, B, C, and D.

SAMPLE	Mass of Glass + Film (mg)	Mass of glass (mg)	Mass difference (mg)	Area covered by film (cm^2)	Thickness of the film (nm)
A	4.912	4.885	0.027	11.25	2.49
B	4.920	4.883	0.037	9.50	4.04
C	4.917	4.885	0.032	9.00	3.69
D	4.920	4.883	0.037	9.60	4.01

THEORETICAL CONSIDERATIONS AND CALCULATION

The thickness of thin films was determined using the Equation 1 below:

$$t = \frac{M}{2AD} \quad \textbf{(1)}$$

where $M = M_2 - M_1$ and M_1 = mass of substrate before deposition, M_2 = mass of substrate after deposition, A = Area covered by the films, D = Density of the CdS thin film ($4.82 g/cm^3$).

The transmittance (T) can be determined from the relationship between measured absorbance (A) of the sample films and transmittance by:

$$A = \log\left(\frac{1}{T}\right) \quad \textbf{(2)}$$

where $T = I/I_o$, I is the transmitted light and I_o is the incident light (Pankove, 1971; Gray, 1982; Cothian, 1958). The absorbance (A), transmittance (T) and reflectance (R) satisfy the law of conservation of energy by the equation (Furlan, et al 1989):

$$A + R + T = 1 \quad \textbf{(3)}$$

The normal reflectance (R) and refractive index (n) are related by the equation (Gittleman, et al 1979) given by:

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \quad \textbf{(4)}$$

The absorption coefficient (α) are related with absorbance and thin film thickness using Beer Lambert's formula (Islam and Podder, 2009) given by:

$$\alpha = 2.303\left(\frac{A}{d}\right) \quad \textbf{(5)}$$

The coefficient of absorption (α) is also related to coefficient of extinction (K) by:

$$\alpha = 4\pi K/\lambda \quad \textbf{(6)}$$

where λ is the wavelength of radiation (Suzuki, et al 1995; Gray, 1982). Near the absorption edge, absorption coefficient (α) is related to band gap (E_g) by:

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \quad \textbf{(7)}$$

where hv is photon energy and n is constant for a given transition equal to ½ for allowed direct band gap semiconductor. The band gap was obtained from allowed direct transition by plotting $\alpha^2 h\upsilon$ against hv and extrapolating the graph to the point where α = 0 is known as energy band gap.

The mean size of the crystallites was determined from X-ray diffraction data. Using the Scherer formula, (Metin, et al., 2008) given by:

$$D_{hkl} = \frac{K\lambda}{\beta cos\theta} \quad \textbf{(8)}$$

where K is a constant, β is FWHM in radians, λ is the wavelength of X-ray used, θ is the Bragg's angle and K value is taken as 0.9 for the calculations.

CHARACTERIZATION OF CdS FILMS

Several techniques were used for the optical and structural characterization of the films, these techniques are described below.

(i) The thickness of as-grown films was determined by the gravimetric method using Mettler Toledo (PB 303) analytical balance.

(ii) The optical absorption spectra of the film were obtained in the UV/VIS/VIR region up to 1100nm using Gen way 6405 UV-spectrophotometer at room temperature and blank measurement was performed on glass substrates as baseline spectra. Other optical and solid-state properties were obtained from the spectra data by calculations based on the theory.

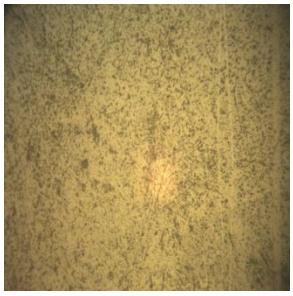
(iii) The surface microstructure of the films was viewed using AP200 MTI optical microscope at magnification 200x.

(iv) The CdS films were characterized by x-ray diffraction techniques in the range of scanning angle 20^0-70^0, current 30mA and voltage 45KV with CuK_α

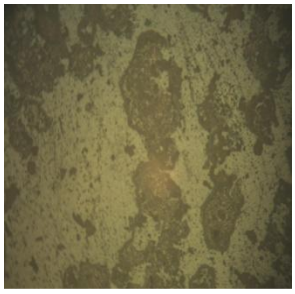
radiation (λ=1.5406Å) using Radicon MD 10 mini diffractometer.

RESULTS AND DISCUSSION

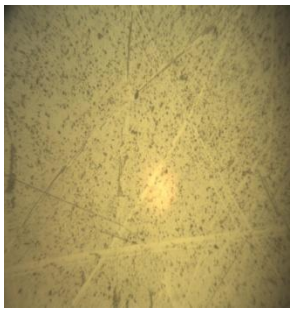
In Figure 1, the optical micrographs of the CdS films at magnification of 200x are shown for all the four samples. From the optical micrograph, we can see that the best homogeneous, smooth and continuous films were obtained using bath composition in sample A and C. Sample C showed a better yellowish color, consistent with the source.



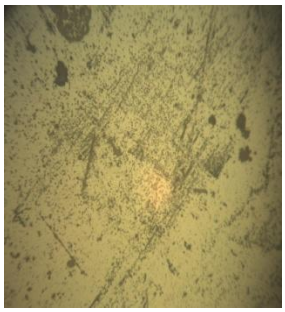
Optical Micrograph of sample A



Optical Micrograph of sample B



Optical Micrograph of sample C



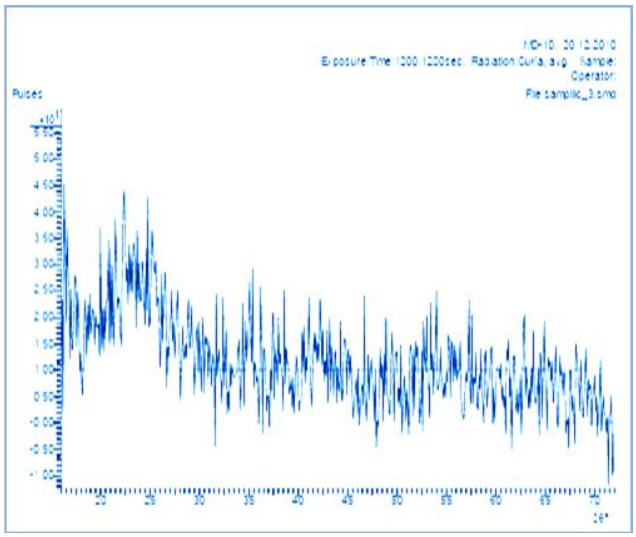
Optical Micrograph of sample D

Figure 1: Optical Micrograph of CdS Thin Films at Different Bath Compositions.

Figure 2 shows the X-ray diffraction patterns of the as-grown thin films samples. It shows the pulses (in arbitrary unit) versus 2θ (diffraction angle). The broad hump in the range $2\theta=20^0$-70^0 is due to the amorphous glass substrate. The planes (001), (002), (042), (107) and (004) indicate the covellite phase with hexagonal crystal structure.

It is seen from the XRD patterns that the CdS films are polycrystalline with orientation along different planes and phases. This result is in agreement with the literature (Metin et al, 2008; Ezema et al, 2010). The grain size of as-grown CdS films was evaluated to be between 12.9nm to 15.4nm by using the Debye Scherrer's formula.

Figure 2: XRD Pattern for the As-Grown CdS.



films at Different Bath Composition.

For the as-grown samples, the interplanar spacing (d_{hkl}) values and (hkl) miller indices for all samples are shown in Table 3.

Table 3: Comparison between XRD Data from the Non-Annealed Sample Prepared with Different Bath Compositions.

Position of peaks	Muller indices	Interplanar Spacing	The relative intensity for non-annealed samples with different bath compositions
2θ	hkl	d_{hkl} (Å)	
24.4	001	3.661	62.3
26.6	002	3.3505	33.1
28.1	042	3.1804	69.2
28.5	214	3.1395	49.1
36.7	530	2.3676	32.2
43.8	107	2.2716	47.2
51.0	800	1.8084	16.3
51.9	080	1.7556	9.9
52.9	181	1.7304	14.9
54.6	004	1.6796	29.4
66.8	2210	1.4028	26.0
69.8	718	1.3473	27.7
70.4	3102	1.3379	29.9
71.0	1040	1.3309	11.9

Figure 3 shows the optical transmission spectra of the CdS films for the four samples. The transmittance is generally high between wavelengths of 500- 1100nm with a gradual fall near the fundamental absorption region. The sample C has the highest average transmission value of about 67.8%.

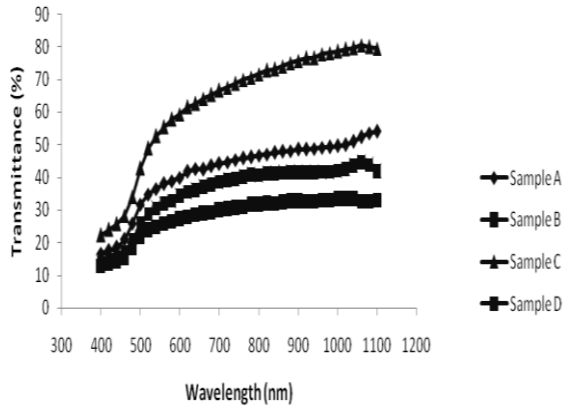


Figure 3: The Transmission Spectra for CdS Films at Different Bath Compositions.

In Figure 4, the absorption spectra of a CBD-CdS sample (in Table 1) is presented. The spectra reveal that the deposited films have low absorbance in the VIS/NIR regions whereas the absorbance is high in the UV region for all the four samples. In general, the absorbance of the films decreases with increasing wavelength and decreasing photon energy. For each sample there is an absorption level that differs from the other.

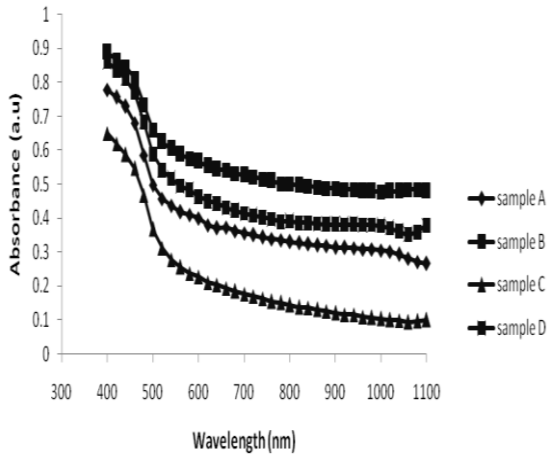


Figure 4: The Absorption Spectra for CdS Films at Different Bath Compositions.

Figure 5 shows the variation of reflectance of the CdS films against wavelength for all the four samples. The reflectance is high in the wavelength range of 400 – 550 nm and a gradual fall in the reflectance in the wavelength range of 600 – 1100 nm was observed.

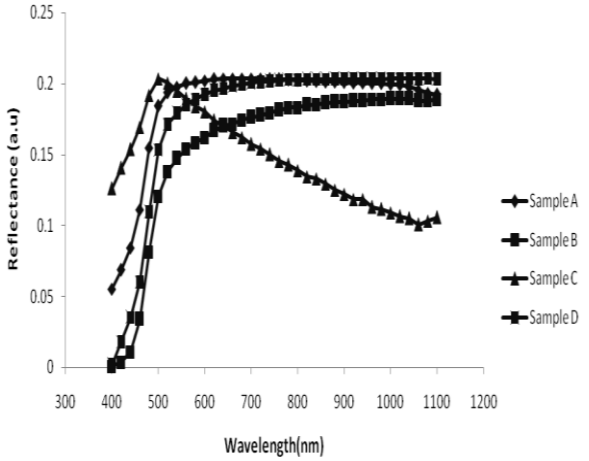


Figure 5: The Reflectance Spectra for CdS Films at Different Bath Compositions.

In Figure 6, the variations of absorption coefficient (α) with photon energy for CdS thin films for all the four samples are shown. From the result, it reveals that there is a gradual increase in the absorption coefficient with increase photon energy for all the samples.

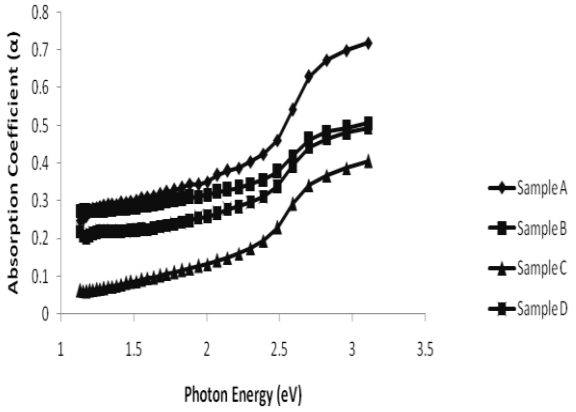


Figure 6: Variation of Absorption Coefficient against Photon Energy for CdS Thin Film at Different Bath Composition.

The energy band gap of CdS thin films for all the samples were calculated with the help of the optical absorption measurement. The theory of interband absorption shows that at optical absorption edge, the absorption coefficient α varies with the photon energy hv according to (Kalman et al., 1973).

We determine the energy band gap by plotting $(\alpha hv)^{1/2}$ versus hv whose intercept on the energy axis gives the energy band gap E_g as shown in Figure 7. The optical band gap for sample A, B, C and D are 2.38eV, 2.45 eV, 2.43 eV and 2.80 eV respectively. These values obtained are in agreement to the previous studies by (Ximello-Quiebras et al, 2004). These results also compare well with 2.40 eV for CdS films reported by (Lazada-Morales et al,, 1998).

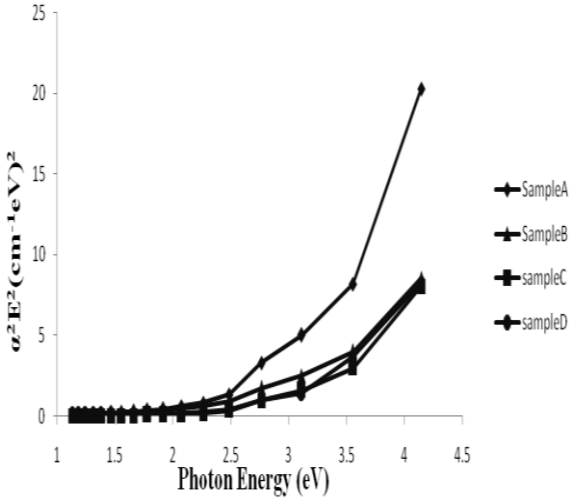


Figure 7: Graph of α^2E^2 against Photon Energy for CdS Films at Different Bath Compositions.

Figure 8 is the variation of extinction coefficient of the CdS film against wavelength for all the four samples. The extinction coefficient is high in the wavelength range of 350 – 450 nm and low in the wavelength range of 400 – 1000 nm. The fall in the extinction coefficient may be due to the absorption of light at the grain boundary (Islam and Podder, 2009).

Figure 9 shows the variation of refractive index against photon energy of the CdS film for all the four samples. From the result, it shows that there is increase in the refractive index in the photon energy range of 1.0 eV to 2.5 eV and there is generally a gradual fall in refractive index at the photon energy range of 2.6 eV to 3.2 eV.

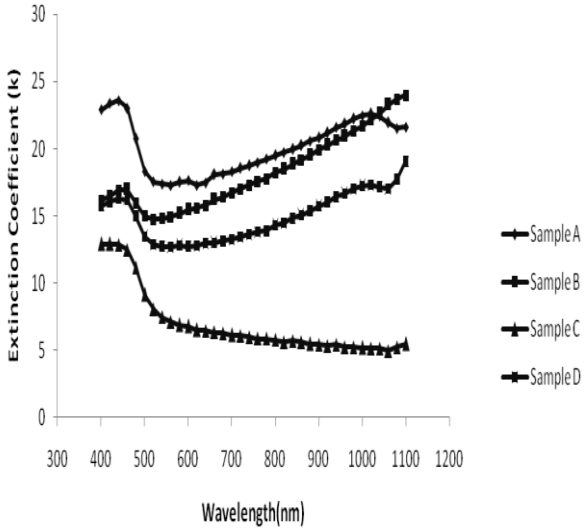


Figure 8: Variation of Extinction Coefficient against Wavelengths for CdS Films at Different Bath Compositions.

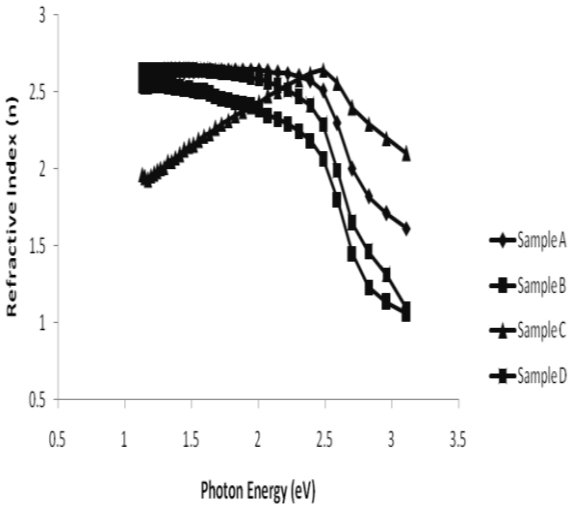


Figure 9: Variation of Refractive Index against Photon Energy for Thin Films at Different Bath Compositions.

CONCLUSION

Optimal CdS thin films were grown by using the CBD technique. The effects of different bath compositions on the optical and structural properties have been investigated.

Different values of optical and solid-state properties were obtained at various bath compositions. Based on our results, we can conclude that physical characteristics of chemically deposited CdS films can be enhanced by controlling the bath composition.

We are very confident that the properties of films presented have good characteristic to be used as a window layer for photovoltaic applications.

ACKNOWLEDGEMENT

The authors acknowledge the efforts of the Centre for Energy Research and Development, OAU and Engineering Material Development Institute, Akure for optical measurements and XRD characterization. We are also thankful to Mr. T.A. Salami of the Lautech Research laboratory for chemical preparation and to the Department of Science Laboratory Technology, Lautech, for providing research facilities for carrying out this work.

REFERENCES

1. Charles, K. 1996. *Introduction to Solid State Physics*. Seventh Edition, John Wiley & Sons: New York, NY. 201.

2. Chaure, N.B, J. Haigh, and I.M. Dharmadasa. Thin Solid Films. John Wiley & Sons: New York, NY. 437 10-17.

3. Cothian, G.F. 1958. *Absorption Spectrophotometry, 2nd Edition*. Hilger and Watts, Ltd. London. UK.

4. Das V.D, J. Sathyanarayanan, and L. Damodare. 1997. "Effect of Annealing and Surface Treatment on the Efficiency of Photoelectrochemical (PEC) Solar Cells with Vacuum Deposited n-InSe Thin Film Electrode". *Surf.Coat.Technol*. 94-95, 669-671.

5. Dharmadasa I.M and J. Haigh. 2006. "Strengths and Advantages of Electrodeposition as a Semiconductor Growth Technique for Applications in Macroelectronic Devices". *Journal of the Electrochemical Society*. 153 G74-G52.

6. Enriquez J.P. and X. Mathew. 2003. "Influences of the thickness on structural, Optical and Electrical properties of Chemical Bath Deposition CdS Thin Films". *Solar Energy Materials & Solar Cells*. 76:313-322.

7. Ezema F.I, S.C. Ezugwu, R.U. Osuji, P.U. Asogwa, B.A. Ezekoye, A.B.C. Ekwealor, and M.P. Ogbu. 2010. "Role of Thermal Annealing on the Optical and Solid State Properties of Chemically Deposited Cadmium Sulphide Nanocrystalline Thin Film Grown in a Polymer Matrix. *Journal of Non-Oxide Glasses.* 1(1):45-50.

8. Furlan, G., D. Nobili, A.M. Sayigh, and B.O. Seraphin (eds.). 1989. *Workshop on Materials Science and the Physics of Non-Conventional Energy Sources*. World Scientific: Singapore.

9. Gittleman, J.I, E.K. Sachel, and Y. Arise. 1979. *Solar Energy Mater*. 1, 93.

10. Gray, D.E. (ed.). 1982. *American Institute of Physics Handbook*. 3rd Edition. McGraw-Hill: New York, NY.

11. Kadirgan, F., D. Mao, W. Song, T. Ohno, and B. McCandless. 2000. "Properties of Electrodeposited Cadmium Sulfide Films for Photovoltaic Devices With Comparison to CdS Films prepared by Other Methods". *Turk J. Chem.* 24:21-33.

12. Kale S.S., R.S. Mane, C.D. Lokhande, K.C. Nandi, and S.H. Han. 2006. "A Comparative Photoelectrochemical Study of Compact In_2O_3/In_2S_3 Multilayer Thin Films". *Materials Science and Engineering B-Solid State Materials for Advanced Technology*. 133(1-3):222-225.

13. Kalman V. and E.W. Nufield. 1973. *Acta Crystallogr*. B 29:2528.

14. Lozada-Morales, R., M. Rubin-Falfan, O. Zela-Angel, and R. Ramirez-Bon. 1998. *J.Phys. Chm. Solid*. 59(9):1393.

15. Mahesha M.G., V.B. Kasturi. and G.K. Shivakumar. 2008. *Turk. J. Phys.* 32:151.

16. Mane R.S and C.D. Lokhande. 2000. *Mater. Chem. Physics* 65:1.

17. Metin, H., F. Sat, S. Erat, and M. Ari. 2008. "Cadmium Sulphide Thin Films Grown by CBD: The Effect of Thermal Annealing on the Structural, Electrical and Optical Properties". *Journal of Optoelectronics and Advanced Materials*. 10(10):2622-2630.

18. Mirmohseni, A., D. Farshbaf, and M. Zarrabi. 2004 "Electrdeposition Coating of Epoxy Resin on Phosphated Steel: Optimization of Key Factors". *International Journal of Polymeric Materials.* 12: 621-632.

19. Nair, P.K., M.T.S. Nair, A. Fermaardex, and M. Ocampo. 1989. *J. Phys.D Appl. Phys*. 22:829.

20. Nikumbh, M., V. Gore, and R.B. Gore. 1997. “Structural, Optical and Photoelectrochemical Studies of the Cadmium Sulfide Films Grown by Chemical Bath Deposition”. *Renew. Energy*. 11: 459-467.

21. Oladeji, I. and I. Chow. 1997. *J. Electro Chem. Soc.* 144: 2342.

22. Ortega-Borges, R. and D. Lincot. 1993. *Electro Chem. J. Soc*. 140:3464.

23. Pankove, J.I. 1971. *Optical Processes in Semiconductors*. Prentice Hall: New York, NY.

24. Raji, P., C. Sanjeeviraja, and C. Ramachandran. 2005. “Thermal and Structural Properties of Spray Pyrolysed CdS Thin Film”. *Indian Academy of Sciences*. 233:233-238.

25. Ramaiah, K.S., R.D. Pilkington, A.E. Hill, R.D. Tomlinson, and A.K. Bhatnagar. 2001. “Structural and Optical Investigations on CdS Thin Films Grown by Chemical Bath Technique”. *Mater. Chem. Phys.* 68: 22-30.

26. Smits FM. 1958. “Measurement of Sheet Resistivities with the Four-Point Probe”. *The Bell Sys.Tech. J.* 711.

27. Thomas, L.F. 1999. *Electronic Devices, Fifth Edition*. Prentice-Hall: Upper Saddle River, NJ. 5-7.

28. Tomas, S.A., O. Vigil, J.J. Alvarado-Gil, R. Lozada-Morales, R. Zelaya-Angel, O.H. Varges, and A.J. Da Silva. 1995. *Applied Physics*. 78:2204.

29. Tsai C., D. Chuu, G. Chen, and S. Yang. 1996. *J. Appl. Phys.* 79:9105.

30. Ugwu, I.E. and D.U. Onah. 2007. Pacific Journal of Science and Technology. 8:160.

31. Wu, X., J. Keane, R. Dhere, D. Dehart, D. Albin, A. Duda, T. Gessert, S. Asher, D. Levi, and P. Sheldon. 2001. *Proceedings of the 17th European Photovoltaic Solar Energy Conference*. Munich, Germany. October 22-26. 995.

32. Ximello-Quiebras, J.N., G. Contreras-Puente, J. Aguilar-Hermández, G. Santana-Rodriguez, and A. Arias-Carbajal Readigos. 2004. “Physical Properties of Chemical Bath Deposited CdS Thin Films”. *Sol. Energy Mater. Sol. Cells*. 82:263-268.

33. Zelaya-Angel, O, J.J. Alvarado-Gil, R. Lozada-Morales, R. Vargas, and F.H. Da Silva. 1994. *A., Applied Physics Lett*. 64:291.

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SUGGESTED CITATION

Awodugba, A.O. and O. Adedokun. 2011. “On the Physical and Optical Characteristics of CdS Thin Films Deposited by the Chemical Bath Deposition Technique”. *Pacific Journal of Science and Technology*. 12(2):334-341.

Pacific Journal of Science and Technology